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A test method for halogenated hydrocarbons has been evaluated and information is provided for the user. Four compounds were investigated, carbon tetrachloride, ethylene dichloride, tetrachloroethylene and trichloroethylene. The subject compounds remained stable in compressed gas mixtures in aluminum and steel cylinders for 4 months. In Tedlar bags held at ambient temperatures, carbon tetrachloride and tetrachloroethylene remained stable for 10 days, trichloroethylene for 2 days, and ethylene dichloride for one day. Heating causes decreases in stabilities. A procedure was developed to remove persistent residues from Tedlar bags that had contacted high concentrations of halogenated hydrocarbons. Information is also included on gas chromatographic columns for use in this method of analysis.

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CCl_4, $C_2H_4Cl_2$, C_2Cl_4,
and C_2HCl_3

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EVALUATION OF EMISSION TEST METHODS FOR HALOGENATED HYDROCARBONS - VOLUME I, CCl_4, $C_2H_4Cl_2$, C_2Cl_4 an C_2HCl_3

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ABSTRACT

Carbon tetrachloride, ethylene dichloride, tetrachloroethylene, and trichloroethylene in compressed gas mixtures stored in aluminum and steel cylinders remained stable for 4 months when maintained at ambient temperatures. Tedlar bags were also evaluated as containers for gaseous mixtures of these four compounds at source-level concentrations. Carbon tetrachloride and tetrachloroethylene samples remained stable for 10 days, trichloroethylene for 2 days, and ethylene dichloride for 1 day. Storage at -25°C did not cause concentration changes; heating did cause changes. When Tedlar bags containing the subject gas mixtures were heated to 70°C, carbon tetrachloride, tetrachloroethylene, and trichloroethylene samples remained stable for 64, 8, and 5 hr, respectively. Heating ethylene dichloride gas mixtures in Tedlar bags to 60°C caused important concentration changes after only 1 hr. A procedure was developed to remove persistent residues from Tedlar bags that had contacted high concentrations of halo-genated hydrocarbons. This procedure consisted of flushing the bag with nitrogen, heating to 60°C, and flushing again. Only residues of ethylene dichloride could not be removed by this technique. Retention indices of several columns that may be used for the analysis of chlorinated hydrocarbons were also determined.

CONTENTS

Abstract iii

Figures v

Tables . . . . . vi-vii

Abbreviations and Symbols viii

Acknowledgment ix

1. Introduction 1

2. Conclusions 4

3. Experimental 6

4. Results and Discussion 10

References 36

FIGURE

Number		Page
1	Double Tedlar bag assembly	9

TABLES

Number		Page
1A	Time Variation of Concentrations of Chlorinated Hydrocarbons in Cylinders	11
1B	Time Variation of Concentrations of Chlorinated Hydrocarbons in Cylinders	12
2	Measured Rates of Concentration Change of Chlorinated Hydrocarbon Cylinder Gases	13
3	Variation of CCl_4 Concentration of Gas Mixture Stored in Tedlar Bags at Ambient Temperatures	22
4	Variation of C_2Cl_4 Concentration of Gas Mixtures Stored in Tedlar Bags at Ambient Temperatures	23
5	Variation of C_2CHl_3 Concentration of Gas Mixtures Stored in Tedlar Bags at Ambient Temperatures	24
6	Variation of $C_2H_4Cl_2$ Concentration of Gas Mixtures Stored in Tedlar Bags at Ambient Temperatures	25
7	Effect of Temperature on Chlorinated Hydrocarbon Concentration of Gas Mixtures Stored in Tedlar Bags	26
8	"Memory" Effects in Tedlar Bags Resulting from High Concentrations of Chlorinated Hydrocarbons	27
9	Variation of $C_2H_4Cl_2$ Concentration of a Gas Mixture in a Double Tedlar Bag	28
10	Kovats Retention Indices of Selected Compounds on 20% SP-2100/0.1% Carbowax 1500 on 100/200 Mesh Supelcoport in 15-Ft x 1/8-In Stainless Steel at 70°C	29-30
11	Kovats Retention Indices of Selected Compounds on Carbopak C-HT, 80/100 Mesh In 6.5-Ft x 1/8-In Stainless Steel at 90°C.	31
12	Kovats Retention Indices of Selected Compounds on 10% FFAP on 80/100 Mesh Acid-Washed Chromasorb W In 20-Ft x 1/8-In Stainless Steel at 125°C	32

TABLES

Number		Page
13	Kovats Retention Indices of Selected Compounds on Porapak T, 80/100 Mesh in 6.5-Ft x 1/8-In Stainless Steel at 140°C	33
14	Kovats Retention Indices of Selected Compounds on 15% Tetracyanoethylated Pentaerythritol on 60/80 Mesh Chromasorb P AW In 16-Ft x 1/8-In Stainless Steel. . . .	34-35

LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

°C	-	degree Celsius
EPA	-	U.S. Environmental Protection Agency
ft	-	foot
hr	-	hour
i.d.	-	inside diameter
in	-	inch
µl	-	microliter
ml	-	milliliter
min	-	minute
OAQPS	-	Office of Air Quality Planning and Standards
o.d.	-	outside diameter
ppm	-	part per million

SYMBOLS

CCl_4	-	carbon tetrachloride
C_2Cl_4	-	tetrachloroethylene
C_2HCl_3	-	trichloroethylene
$C_2H_4Cl_2$	-	ethylene dichloride
N_2	-	nitrogen

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SECTION 1

INTRODUCTION

Under the 1976 Toxic Substances Control Act, the U.S. Environmental Protection Agency (EPA) is given responsibility to test chemicals for health and environmental effects. Recently, an interagency panel selected certain categories of chemicals to be given high priority; the halogenated hydrocarbons were designated as one such category (1). After screening many halogenated hydrocarbons on the basis of degree of genotoxicity, production volume, and potential for human exposure, a special task force prepared a list of compounds for immediate attention (2). These compounds include carbon tetrachloride (CCl_4), ethylene dichloride ($C_2H_4Cl_2$), tetrachloroethylene (C_2Cl_4), and trichloroethylene (C_2HCl_3).

An essential feature in pollution assessment and control is development of an accurate source test method to measure amounts of emissions and to determine the efficacy of control technology. For this purpose, a Tentative Method was formulated in the Emission Measurement Branch, Emission Standards and Engineering Division, Office of Air Quality Planning and Standards (OAQPS) (see Appendix A). The present study was undertaken to evaluate this method and to provide information to aid the user.

The test method under consideration involves collection in Tedlar bags and analysis by gas chromatography with flame ionization detection. The use of bottled gas mixtures is one calibration option. The ability of Tedlar bags to preserve gas samples free from contamination and change has been

the subject of many studies. Seila et al. (3) reviewed recent work in this area and studied the effects of simulated sunlight on stability of hydrocarbon samples at ambient concentrations in Tedlar bags. They observed a series of contamination peaks released by the radiation and suggested that the origin of these peaks was manufacturing residues. In addition, Tedlar bags also have been used for source sampling. In this field, samples usually contain much higher concentrations, and the major problems result from sample cross-contamination and from the extremes of temperature that are encountered. Tedlar bags have been successfully employed in the source sampling method for vinyl chloride (4). Further, a recent study in this laboratory (5) dealt with the stability of benzene-containing gas mixtures in Tedlar bags over a range of temperatures. It showed that benzene is quite stable in Tedlar and relatively free from "memory" effects. The present investigation was carried out to obtain information on the stability of gas mixtures in Tedlar bags containing the four chlorinated hydrocarbons of interest.

Cylinders of compressed gases are often used as secondary standards during measurements in the field, where they are more convenient than permeation tubes or diluted gas preparations. Therefore, this study also examined the stability of compressed gases containing CCl_4, $C_2H_4Cl_2$, C_2HCl_3, and C_2Cl_4 in cylinders. The stability of these compounds under such conditions has received only limited attention in the past (6). Further, the present investigation included an evaluation of the gas chromatographic column recommended in the Tentative Method for Analysis of Halogenated hydrocarbons. Several other columns were also examined to provide analysts with alternatives when interfering compounds are present.

This work was carried out in the Source Section of the Quality Assurance Branch, Environmental Monitoring and Support Laboratory, Research Triangle Park, North Carolina, which has a program to evaluate and standardize source emission test methodology. Work is continuing with other halogenated hydrocarbons.

SECTION 2

CONCLUSIONS

Steel cylinders containing CCl_4, $C_2H_4Cl_2$, C_2HCl_3, and C_2Cl_4 in nitrogen (N_2) and aluminum cylinders containing C_2HCl_3 remain stable for 4 months when maintained at ambient temperatures. After that time period, no concentration changes are detected.

Tedlar bags may be used to contain mixtures of halogenated hydrocarbons in N_2 at source-level concentrations. When held at ambient temperatures, CCl_4 remains stable for at least 10 days, C_2Cl_4 for 10 days, C_2HCl_3 for 2 days, and $C_2H_4Cl_2$ for 1 day.

Storage at -25°C in Tedlar bags for 16 hr does not cause changes in concentrations of any of the four halogenated hydrocarbons, provided that temperature is maintained above the dew point.

When Tedlar bags containing the subject gas mixtures are heated to 70°C, CCl_4, C_2HCl_3, and C_2Cl_4 remain stable for 64, 8, and 5 hr, respectively. Heating Tedlar bags containing $C_2H_4Cl_2$ to 60°C causes the concentration to decrease after only 1 hr. Therefore, steps should be taken to cool high-temperature gas streams when sampling for $C_2H_4Cl_2$ and employing Tedlar bags.

The introduction of high concentrations of halogenated hydrocarbons into Tedlar bags causes formation of persistent residues that may contaminate subsequent samples. A decontamination procedure was employed that consisted of flushing the bag with N_2, heating to 60°C for 1 hr, and flushing again. Bags contaminated with CCl_4 and C_2Cl_4 can be decontaminated with one such

treatment; C_2HCl_3 requires two and $C_2H_4Cl_2$ cannot be decontaminated by this method.

At ambient temperatures $C_2H_4Cl_2$ tends to be absorbed into the plastic; at 60°C it permeates through the plastic.

The chromatographic column recommended in the Tentative Method for the Analysis of Halogenated Hydrocarbons from Stationary Sources achieves excellent separations with the four compounds of interest. Other columns are also available for use under special circumstances.

SECTION 3

EXPERIMENTAL

Tedlar bags were fabricated from 2-mil plastic sheets. The edges were sealed with a Vertrod Thermal Impulse Heat Sealing Machine (Model 48 EPS 1/4 WC). Connections to the bag were made using an O-Seal Straight Thread Adapter with 0.25-in o.d. tube and a 7/16-20 thread (Swagelok 401-A-OR) which was inserted through a 2-in-square piece of VisQueen polyethylene tape fixed to the outside surface of the bag. The adapter was held in place with a 0.058-in Teflon washer (0.5 in i.d. x 1-in o.d.) and a 7/16-20 nut. A 7115G4B Hoke ball valve was connected to the adapter.

Cylinders containing gaseous mixtures of N_2 and the chlorinated hydrocarbons under investigation were obtained from Airco, Inc. (Research Triangle Park, North Carolina). Hydrocarbon concentrations were determined using Tedlar bag calibration standards by injection of the liquid compound while filling the bags with N_2. The N_2 was measured using a No. 802 Singer dry gas meter; a No. 801, 10-ul Hamilton syringe was used to measure the compounds of interest. In other instances, Tedlar bags were filled directly from the reference cylinders.

Chlorinated hydrocarbon concentrations were determined using a Hewlett-Packard Model 5830A gas chromatograph equipped with dual flame ionization detectors and a 0.1-ml sampling loop. A Hewlett-Packard Model 18850A integrating terminal was employed to record output. The chromatographic column consisted of a 15-ft x 1/8 in stainless steel helix packed with 20%

SP-2100/0.1% Carbowax 1500 on 100/200-mesh Supelcoport. The following operating conditions were employed: inlet temperature, 250°C; column, 75°C; detector, 300°C; carrier gas, liquid air N_2 at 20 ml/min. Under these conditions, only a single peak could be observed in each compound of interest. Tedlar bags were sampled by drawing the gas through the chromatographic sampling loop using the house vacuum. Bottled gases were forced through the sampling system under their own pressures. A benzene gas mixture was used to normalize the gas chromatograph results.

In several instances, gas samples containing high concentrations of the subject compounds were introduced into Tedlar bags. These atmospheres were prepared by slowly passing N_2 gas through an impinger containing the liquid compound under study. The concentration was calculated for the saturation vapor pressure of the chlorinated hydrocarbon at 0°C, the temperature at which the impinger was maintained. This temperature was chosen to assure that condensation would not take place in the bag during the subsequent study.

To study the effusion of chlorinated hydrocarbons through Tedlar plastic, a double bag assembly was constructed. This consisted of an inner bag housed in an outer bag of approximately twice the volume, so that when the inner bag was filled with a chlorinated hydrocarbon gas mixture, the outer bag could be filled with an equivalent volume of pure N_2. This assembly was employed in a previous study in this laboratory (5) and is illustrated in Figure 1.

Retention indices were determined for several chlorinated hydrocarbons and a number of other selected compounds on five chromatographic columns. The columns were:

Carbopak C-HT, 80/100 mesh in 6.5-ft x 1/8 in stainless steel.

10% FFAP on 80/100 mesh acid-washed Chromasorb W in 20-ft x 1/8 in

stainless steel.

Porapak T, 80/100 mesh in 6.5-ft. x 1/8-in stainless steel.

20% SP-2100/0.1% Carbowax 1500 on 100/120 mesh Supelcoport in 15-ft x 1/8-in stainless steel.

15% tetracyanoethylated pentaerythritol on 60/80 mesh Chromasorb P AW in 16-ft x 1/8-in stainless steel.

The columns were obtained from Supelco, Inc. (Belefonte, Pennsylvania) and were conditioned overnight at a temperature and flow rate recommended by the manufacturer. The compounds under investigation were used without further purification.

Relative retentions in Kovats retention index units (7) were obtained from chromatograms of suitable mixtures containing n-alkanes as internal standards. Retention distances measured between point of injection and peak maxima were corrected for the column gas holdup volume by means of retention of methane (8). The adjusted retentions were then used to calculate values for the retention index by means of the expression recommended by the Chromatography Discussion Group (9):

$$I = 100\,N + 100\,n\,\frac{\log R_X - \log R_N}{\log R_{N+n} - \log R_N}$$

where R_X, R_N, and R_{N+n} are the adjusted retentions of the solute and n-alkanes containing N and N+n carbon atoms, respectively.

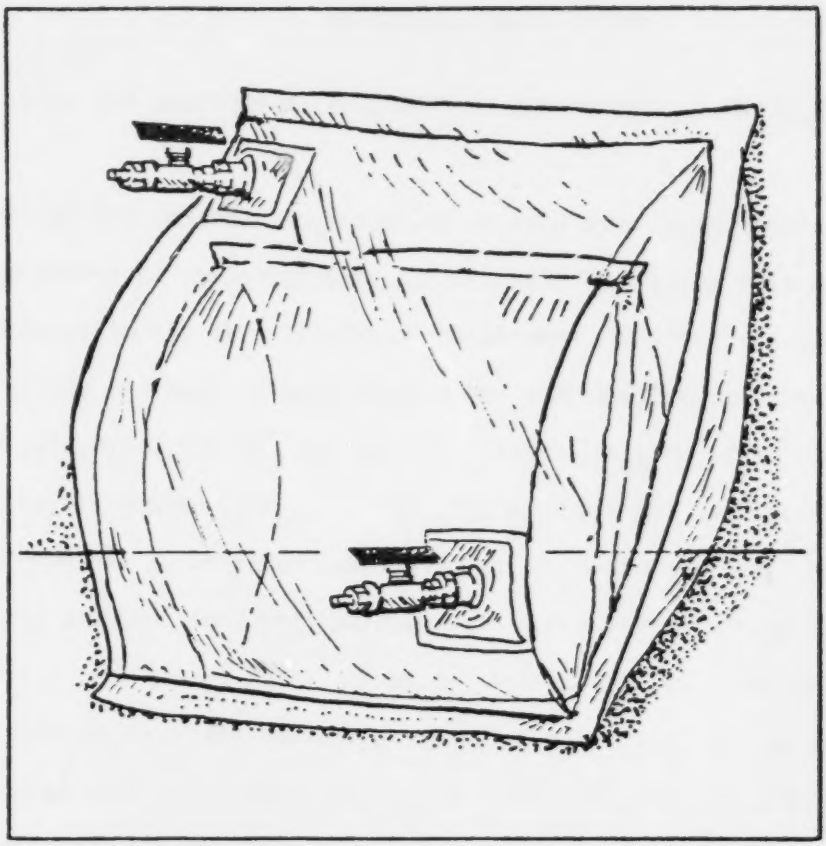

Figure 1. Double Tedlar Bag Assembly.

SECTION 4

RESULTS AND DISCUSSION

(STABILITY OF CHLORINATED HYDROCARBON GAS MIXTURES IN ALUMINUM AND STEEL CYLINDERS)

Because cylinder gases were used as calibration standards for our Tedlar bag studies, and also because of plans to use such cylinders in future quality assurance programs, a study was undertaken to determine if gas mixtures containing the chlorinated hydrocarbons under investigation remained stable in bottled gas containers. A single steel cylinder each of CCl_4, $C_2H_4Cl_2$, and C_2Cl_4, and two steel and two aluminum cylinders of C_2HCl_3 were employed. In each case, the diluent gas was N_2. The gases were measured at various intervals over a period of approximately 4 months, counting time from the date of cylinder preparation. The results are listed in Tables 1A and 1B. A stability test was carried out by performing a linear regression analysis on each data set and calculating the time variation of the concentration. This latter quantity was judged to be significant if its magnitude exceeded its standard deviation by at least a factor of 3. The results of these analyses are listed in Table 2. Since in each instance the calculated rate of change was not measurably different from 0, the cylinder gases met the test for stability. However, a concentration change was observed in the $C_2H_4Cl_2$ cylinder and in one C_2HCl_3 steel cylinder. The first point in each data set deviated considerably from the subsequent values, indicating that the concentration underwent a decrease immediately after the cylinder was prepared but then stabilized.

TABLE 1A. TIME VARIATION OF CONCENTRATIONS OF CHLORINATED HYDROCARBONS IN CYLINDERS

Elapsed Time, days*	Concentration, ppm			
	CCl_4 (steel cylinder)	CH_2ClCH_2Cl (steel cylinder)	CCl_2:CCl_2 (steel cylinder)	$CHCl$:CCl_2 (steel cylinder)
7	21.9	14.2	-	19.6
16	20.3	13.3	-	17.6
23	19.9	12.4	18.2	17.8
30	21.1	12.6	19.1	17.2
37	20.3	12.9	18.0	16.5
44	18.5	12.1	19.1	16.4
51	19.0	12.5	18.2	17.3
68	18.2	12.7	20.2	17.6
92	18.6	13.0	20.3	18.3
97	19.4	12.6	19.4	17.6
114	19.5	12.5	18.5	17.7

*From date of filling.

TABLE 1B. TIME VARIATION OF CONCENTRATIONS OF CHLORINATED HYDROCARBONS IN CYLINDERS

Elapsed Time, days*	Concentration, ppm		
	C_2HCl_3 (steel cylinder)	C_2HCl_3 (aluminum cylinder)	C_2HCl_3 (aluminum cylinder)
5	9.7	30.0	11.8
7	9.6	27.9	11.9
25	9.9	31.4	11.1
42	10.1	29.4	11.8
49	9.7	29.1	11.5
63	9.5	28.8	11.8

*From date of filling.

TABLE 2. MEASURED RATES OF CONCENTRATION CHANGE OF CHLORINATED HYDROCARBON CYLINDER GASES

Compound	Cylinder Type	Concentration, ppm	Rate of Change,* %/day	Standard Deviation
CCl_4	Steel	19.7	-0.06	0.04
$C_2H_4Cl_2$	Steel	14.2	-0.01	0.03
C_2Cl_4	Steel	19.0	+0.05	0.05
C_2HCl_3 #1	Steel	19.6	+0.04	0.03
C_2HCl_3 #2	Steel	26.0	-0.02	0.05
C_2HCl_3 #3	Aluminum	78.7	-0.02	0.08
C_2HCl_3 #4	Aluminum	31.1	-0.02	0.05

*The initial point was omitted in calculating the rate of change.

Student's t-test was applied to the data to compare the deviations in question with those that would occur with normal measurement fluctuations. The t-test indicated a probability the deviations resulted from statistical fluctuations of less than 0.01 and 0.025 for $C_2H_4Cl_2$ and the C_2HCl_3, respectively. Thus, there was a correspondingly high probability that the points under consideration were evidence for an initial decrease in concentration. Because of this, both of these points were omitted when linear regression analysis was applied to the data sets in question. The t-test was also applied to the extreme point in each of the other data sets listed in Tables 1A and 1B, with the result that all were within the range of normal measurement fluctuations. Therefore, the data in Tables 1 and 2 are evidence that the gases in the cylinders under study remained stable over a time period of from 2 weeks to as long as 4 months after preparation.

Although stability was demonstrated at ambient temperatures, some evidence was obtained that decay occurs at higher temperatures. One steel and one aluminum cylinder containing C_2HCl_3 were remeasured and heated at 50°C in a Forma Scientific Environmental Chamber. At the end of 14 days, they were brought to room temperature, and when remeasured, the steel and aluminum cylinders measured 90.0±2.1 and 88.5±3.9% of the initial value, respectively. The changes were significant at the 95% confidence level.

STABILITY OF CHLORINATED HYDROCARBON SAMPLES IN TEDLAR BAGS AT AMBIENT TEMPERATURES

The stability of samples of C_2HCl_3, C_2Cl_4, CCl_4, and $C_2H_4Cl_2$ in N_2 stored in Tedlar bags was studied. Several bag samples of each compound were prepared by either filling the bags directly from standard cylinders or by in-

jecting measured amounts of liquid into bags filled with known volumes of N_2. The bags were measured daily over a period of time on a Hewlett-Packard 5830 gas chromatograph and concentrations were determined by comparison with measurements of standard cylinders.

The results of the measurements (Tables 3 through 6) show that CCl_4 was the most stable of the four compounds. The CCl_4 concentrations of two of the three bags remained essentially unchanged for as long as 10 days. Calculations by linear regression of the rate of decay yielded a value that was approximately equal to its standard deviation. The decay rate of the third bag was measurable. The concentration in the third bag decreased by approximately 4% per day; it contained a relatively high concentration of CCl_4, which may have affected the decay rate.

C_2Cl_4 samples stored in Tedlar bags were also fairly stable. Although the concentrations of two of the four bags decreased steadily over a 39-day period, none decayed by more than 10% within 3 days.

Tedlar bag samples of C_2HCl_3 were less stable. Of the four bags prepared, two decayed steadily at an average rate of about 7% per day over an 11-day period. The concentrations of the other two bags were nearly constant over a 14-day period.

$C_2H_4Cl_2$ was the least stable of the four compounds. Two of the bags decayed by approximately 5% in only 1 day. The third bag decayed by approximately 7% over the first 5 days.

The results of this study indicate the lengths of time that samples of the four compounds can be stored in Tedlar bags without significant concentration changes. If an approximate 10% decrease in concentration is considered tolerable, samples of C_2Cl_4 can be stored for up 4 days; low concen-

tration samples of CCl_4 can be stored for 10 days or more. Samples of C_2HCl_3 and $C_2H_4Cl_2$ should be stored for no longer than 2 days and 1 day, respectively.

(STABILITY OF CHLORINATED HYDROCARBON SAMPLES IN TEDLAR BAGS AT TEMPERATURES ABOVE AND BELOW AMBIENT)

Source sampling often must be carried out on heated gas streams or under extreme weather conditions. For these reasons, some information also was obtained about the stability of chlorinated hydrocarbon gas mixtures in Tedlar bags at temperatures above and below ambient. In studying stability at low temperatures, bag samples were stored in a freezer for a period of 16 hr. (In each case, the temperature remained above the dew point of the compound under study.) Bags were then brought to room temperature and measured.

The results (Table 7) show no observable change in the concentrations of the compounds under study. When Tedlar bags were heated, however, some changes were observed. Heating caused the release of some materials from the plastic, but none eluted on the chromatogram at the same times as the compounds of interest. Heating to 60°C caused one $C_2H_4Cl_2$ gas sample to decrease by 6.4% after 1 hr and another to decrease by 9.4%. On the other hand, a C_2Cl_4 sample did not show a measurable change when heated to 60°C for 1 hr, but heating to 70°C for 16 hr did cause a 26% decrease. After heating a C_2HCl_3 sample to 90°C for 1 hr, a 5.3% change was observed. This change was barely within the limit of detection. A 15% decrease was observed at 75°C after 16 hr. In contrast, CCl_4 gas samples were very stable at high temperatures. After heating one sample repeatedly for a total of 63 hr at 70°C, only a 5% change could be detected.

Certain conclusions can be drawn from these results. Gas samples containing the four compounds of interest will not be affected if stored in Tedlar bags at temperatures that are below ambient but above the compound's dew point. Exposure of $C_2H_4Cl_2$ bag samples to temperatures above 60°C should be avoided, even for short periods of time. C_2Cl_4 and C_2HCl_3 samples may be exposed to temperatures of approximately 70°C for a few hours without significant losses. CCl_4 samples may be heated to 70°C for up to 63 hr without undergoing important concentration changes.

MEMORY EFFECTS RESULTING FROM HIGH CONCENTRATIONS

"Memory" effects were studied by subjecting Tedlar bags to concentrations of chlorinated hydrocarbons in the 5,000 to 40,000 ppm range. Such concentrations were employed because they result in correspondingly higher amounts of residuals that are easier to detect. Although high concentrations should not be expected in controlled effluent streams, they often occur as the result of process upsets (4) and may contaminate a Tedlar bag that happens to be in use. Therefore, it was necessary to obtain some information on the magnitude of "memory" effects and to examine decontamination procedures.

To carry out this study, a high-concentration gas sample was prepared for each compound of interest and introduced into a new Tedlar bag. After 1 hr, the bag was evacuated and flushed. The latter was accomplished by filling the bag with gas and evacuating a total of three times. Each bag was then filled N_2 gas, checked to show that all of the chlorinated hydrocarbon had been removed from the gas phase, and left to stand at room temperature for 66 hr. The chlorinated hydrocarbon concentration in each bag was subsequently measured. Following this, each bag was heated for 1 hr at 60°C

and the concentration remeasured. The bag was then flushed and reheated as described above and remeasured. The results are listed in Table 8.

All of the bags that had contacted high concentrations of chlorinated hydrocarbons retained some of these materials and released them into the gas phase when left to stand at room temperature (see Table 8). Upon heating, an additional amount of material was released. In the case of C_2HCl_3 and $C_2H_4Cl_2$, amounts of this were large. When the bags were reflushed and reheated, those that had contained C_2HCl_3 and $C_2H_4Cl_2$ continued to release material, but those that had contained CCl_4 and C_2Cl_4 released only negligible amounts.

The results of this study of high concentrations of chlorinated hydrocarbons may be summarized as follows. Tedlar bags that contact high concentrations retain material even after the sample is removed and the bag is thoroughly flushed. Such residuals can contaminate subsequent samples. Heating to 60°C and flushing with N_2 is sufficient to remove contamination from Tedlar bags that have been filled with 42,000 ppm CCl_4 and 5,700 ppm C_2Cl_4. On the other hand, Tedlar bags filled with 27,000 ppm C_2HCl_3 require two such treatments, and 30,000 ppm C_2HCl_2 cannot be decontaminated by this procedure. These results also show that the order of degree of absorption into Tedlar plastic is $C_2H_4Cl_2 > C_2HCl_3 > C_2Cl_4 > CCl_4$, and is the same as the order found for rates of decay of gaseous samples. Therefore, the results obtained for the absorption of chlorinated hydrocarbons into Tedlar are consistent with our findings about sample decay.

$C_2H_4Cl_2$ GAS MIXTURE IN A DOUBLE TEDLAR BAG

In order to obtain some additional information about the loss of chlorinated hydrocarbons from Tedlar bags, a double bag was employed. This technique is described in Section 3. A mixture of $C_2H_4Cl_2$ in N_2 was placed

in the inner bag and an approximately equal volume of N_2 gas was placed in the outer bag. The $C_2H_4Cl_2$ concentrations in both bags were observed over a 7-day interval. The assembly was then heated to 60°C for 22 hr and the concentration measured over an additional 8 days. The results are shown in Table 9.

Prior to heating, the $C_2H_4Cl_2$ concentration in the inner bag decreased but no $C_2H_4Cl_2$ was detected in the outer bag. Heating caused a further decrease in the inner bag concentration and caused $C_2H_4Cl_2$ to appear in the outer bag. In the subsequent time interval, the $C_2H_4Cl_2$ concentration decreased in both bags. These findings are evidence that the concentration decrease is the result of absorption into the plastic and not effusion through the bag. Heating apparently increases mobility through the plastic and results in the expulsion of some $C_2H_4Cl_2$ from the plastic. This viewpoint is consistent with the fact that contamination can be removed from the bags by heating.

When the data in Table 9 were subjected to kinetic analysis, the first-order rate constants for the changes in the inner bag before and after heating were $-0.012 \pm 0.001\ d^{-1}$ and $-0.011 \pm 0.003\ d^{-1}$, respectively. (The variations are standard deviations.) On the other hand, the corresponding constant for the decay of $C_2H_4Cl_2$ in the outer bag was determined to be $-0.037 \pm 0.009\ d^{-1}$, a difference in magnitude that is statistically significant. It may be assumed, then, that the gas in the outer bag has a greater rate of decay because it is in contact with a greater surface area. Thus, these results are also consistent with the supposition that $C_2H_4Cl_2$ is absorbed into the Tedlar plastic.

SEPARATION OF HALOGENATED HYDROCARBONS BY GAS CHROMATOGRAPHY

The separation of the chlorinated compounds of interest from other substances by gas chromatography was also investigated. The column specified in the Tentative Method for Halogenated Hydrocarbons was studied, along with four others. Relative retentions in Kovats retention index units (7) were determined from the elution times of compounds in suitable mixtures. These calculations are described in Section 3 above; the results are listed in Tables 9 through 13. Tables of retention indices are often used as a guide in selecting chromatographic columns for separating complex mixtures and for making preliminary identifications of components. As a general rule, it is best to have differences of 30 retention units between compounds in order to obtain interference-free measurements.

The column specified in the Tentative Method employs methylsilicone (SP-2100) in the stationary phase. The column separates the four compounds of interest from each other and from many other chlorine-containing compounds (see Table 9). The data also show that there are other potential interferents. However, our present concern is for the use of this column to measure emissions from dry cleaning and metal degreasing operations in which many such interfering compounds would not ordinarily be present. An example of an unlikely interferent is furfural, which has the same retention index as C_2Cl_4 on the column under discussion. On the other hand, it should be noted that the retention indices of $C_2H_4Cl_2$, CCl_4, and C_2HCl_3 fall between 600 and 700, a region in which many gasoline hydrocarbons elute.

Table 11 presents the results obtained using Carbopak C-HT. Carbopak C-HT is a graphitized thermal carbon black that has been treated with hydrogen at 1000°C (10). It is said to have a high resolving power. On this column,

the chlorinated hydrocarbons of interest are well separated and elute with the lighter hydrocarbons. The latter process would be an advantage in resolving the compounds of interest from gasoline hydrocarbons.

The FFAP column is one that has been employed by the National Institute of Occupational Safety and Health for the analysis of organic solvents in air (11). The stationary phase consists of free fatty acid Carbowax 20 M reacted with nitroterephthalic acid. The results (Table 12) show that chlorinated hydrocarbons elute over a wide range of indices. Many of the compounds of interest elute after the gasoline hydrocarbons. $CHCl_3$ and C_2Cl_4 are not well separated.

Porapak T is a porous polymer based on ethyleneglycoldimethacrylate and is reported to possess fair resolving power (10). On this column, many chlorinated hydrocarbons are well separated, except that $C_2H_4Cl_2$ and C_2HCl_3 interfere (see Table 13).

The final column employs tetracyanoethylated pentaerythritol as a stationary phase. It is a highly polar column, and many compounds have retention indices that vary considerably with temperature; others show less variation (see Table 14). With such columns, it is often possible to resolve interfering substances by changing column temperature.

TABLE 3. VARIATION OF CCl_4 CONCENTRATION OF GAS MIXTURE STORED IN TEDLAR BAGS AT AMBIENT TEMPERATURES

Elapsed Time, days*	CCl_4 Concentration, ppm		
	Bag 1	Bag 2	Bag 3
0	9.24	1034	28.8
1	9.52	999	28.9
2	9.55	948	
3	9.28		
4	8.96		
5		936	28.0
6		838	
7	9.23	849	28.0
8	9.21	688	
9	9.27		
10	9.11		

*From date when bags were prepared.

TABLE 4. VARIATION OF C_2Cl_4 CONCENTRATION OF GAS MIXTURES STORED IN TEDLAR BAGS AT AMBIENT TEMPERATURES

Elapsed Time, days*	C_2Cl_4 Concentration, ppm			
	Bag 1	Bag 2	Bag 3	Bag 4
0	19.7	10.9	65.0	32.1
1			63.5	31.7
2			62.2	31.0
3	17.9	10.0	61.6	30.9
4	16.8	9.4	59.2	29.6
5	15.9	9.2		
6	15.5	9.2		
7	14.6	8.8		
25	4.2	4.3		
35			60.2	30.1
36			58.2	29.1
38	2.5	3.9		
39	2.2	3.8		

*From date when bags were prepared.

TABLE 5. VARIATION OF C_2HCl_3 CONCENTRATION OF GAS MIXTURES STORED IN TEDLAR BAGS AT AMBIENT TEMPERATURES

Elapsed Time, days*	C_2HCl_3 Concentration, ppm			
	Bag 1	Bag 2	Bag 3	Bag 4
0	21.3	65.1	16.0	7.0
1				6.6
2				6.9
3	20.0	60.9	15.0	6.0
4	19.7	51.0	14.4	5.5
5	19.9	48.0	15.0	
6	19.7	41.2	14.4	
7	20.0	30.2	15.0	4.3
8				3.7
9				3.1
10	20.4	12.1	15.2	2.3
11	20.0	0.3	15.0	1.1
12	20.0		15.0	
13	20.1		15.0	
14	19.7		14.7	

*From date when bag was prepared.

TABLE 6. VARIATION OF $C_2H_4Cl_2$ CONCENTRATION OF GAS MIXTURES STORED IN TEDLAR BAGS AT AMBIENT TEMPERATURES

Elapsed Time, days*	$C_2H_4Cl_2$ Concentration, ppm		
	Bag 1	Bag 2	Bag 3
0	31.8	6.2	91.9
1	29.9	5.9	
2	28.6	5.5	
5			86.0
6	22.1		
7			83.4
8	19.2	5.3	81.8
9	16.6		80.5
11		4.9	
12			80.1
16			78.2

*From date when bags were prepared.

TABLE 7. EFFECT OF TEMPERATURE ON CHLORINATED HYDROCARBON CONCENTRATION OF GAS MIXTURES STORED IN TEDLAR BAGS

Compound	Sample Number	Temperature, °C	Time, hr	Concentration, ppm		Change, %
				Initial	Final	
CCl_4	1	-25	16	18.7	19.3	103.2
CCl_4	2	75	1	46.6	46.1	98.9
CCl_4	2	70	16	46.6	47.2	101.3
CCl_4	2	70	6	46.6	45.4	97.4
CCl_4	2	70	16	46.6	44.8	96.0
CCl_4	2	70	24	46.6	44.2	94.7
$C_2H_4Cl_2$	1	-41	16	7.35	7.39	100.5
$C_2H_4Cl_2$	2	60	1	7.35	7.25	98.6
$C_2H_4Cl_2$	3	60	1	7.35	6.88	93.6
$C_2H_4Cl_2$	4	60	2	7.35	6.66	90.6
C_2Cl_4	1	-25	16	21.4	21.1	98.8
C_2Cl_4	2	60	1	20.4	20.6	100.5
C_2Cl_4	2	70	16	20.4	15.1	74.0
C_2HCl_3	1	90	1	21.4	20.2	94.7
C_2HCl_3	2	-25	16	21.3	21.8	102.3
C_2HCl_3	2	75	16	21.3	18.1	85.0
C_2HCl_3	3	-25	16	12.9	13.3	103.1

TABLE 8. "MEMORY" EFFECTS IN TEDLAR BAGS RESULTING FROM HIGH CONCENTRATIONS OF CHLORINATED HYDROCARBONS

Compound	Concentration, ppm			
	Initial*	After Flushing	After Heating	After Second Heating**
CCl_4	42,000	8.5	10.7	0.0
C_2Cl_4	5,700	12.5	14.4	0.2
C_2HCl_3	27,500	14.4	65.9	1.4
$C_2H_4Cl_2$	30,100	8.9	185.0	5.4

*Calculated from vapor pressure at 0°C.

**Bag flushed before second heating.

TABLE 9. VARIATION OF $C_2H_4Cl_2$ CONCENTRATION OF A GAS MIXTURE IN A DOUBLE TEDLAR BAG

Elapsed Time, days*	$C_2H_4Cl_2$ Concentration, ppm	
	Inner bag	Outer bag
0	91.0	0.0
5	86.1	0.0
7	83.6	0.0
8	75.5	6.2+
9	73.4	5.7
12	70.0	4.8
16	69.0	4.6

*From date when bag was prepared.

+After heating at 60°C for 22 hr.

TABLE 10. KOVATS RETENTION INDICES OF SELECTED COMPOUNDS ON 20% SP-2100/0.1% CARBOWAX 1500 on 100/200 MESH SUPELCOPORT IN 15-FT X 1/8-IN STAINLESS STEEL AT 70°C

Chlorinated Compound	Index
dichloromethane	516
trans-1,2-dichloroethene	556
1,1-dichloroethane	565
chloroform	606
ethylene dichloride	636
1-chlorobutane	641
carbon tetrachloride	665
trichloroethylene	695
1-chloropentane	746
2-chloropentane	746
1,3-dichloropropane	765
tetrachloroethylene	813
chlorobenzene	842
1,4-dichlorobutane	886
1,2,3-trichloropropane	898
p-chlorotoluene	948

Other Compound	Index
methanol	370
acetaldehyde	374
methyl formate	392
2-propanol	477
diethyl ether	488
methylal	493
formaldehyde	508
ethyl bromide	514
cyclopentene	560
4-methylpentene-1	562
cyclopentane	567
4-methylpentene-2	569
2-methylpentene-1	574
methylethylketone	579
hexene-1	590
methyl acrylate	595

TABLE 10. KOVATS RETENTION INDICES OF SELECTED COMPOUNDS ON 20% SP-2100/0.1% CARBOWAX 1500 on 100/200 MESH SUPELCOPORT IN 15-FT X 1/8-IN STAINLESS STEEL AT 70°C (Continued)

Other Compound	Index
hexane	600*
2-ethylbutene-1	600
2,2-dimethylpentane	621
crotonaldehyde	629
methylcyclopentane	633
1-butanol	649
methylcyclopentene	654
benzene	658
3,3-dimethylpentane	660
thiophene	663
cyclohexane	667
2-pentanone	668
2,3-dimethylpentane	672
3-pentanone	677
cyclohexene	683
heptene-1	689
heptane	700*
1,4-dioxane	721
methylisobutylketone	722
methylcyclohexane	728
pyridine	733
toluene	761
methylcyclopentene	770
butyl acetate	795
octane	800*
furfural	813
amyl acetate	860
ethylbenzene	869
m-xylene	876
p-xylene	877
nonane	900*
o-xylene	900
decane	1000*
naphthalene	1182

*Used as a standard.

TABLE 11. KOVATS RETENTION INDICES OF SELECTED COMPOUNDS ON CARBOPAK C-HT, 80/100 MESH IN 6.5-FT X 1/8-IN STAINLESS STEEL AT 90°C

Chlorinated Compound	Index
1,1-dichloroethane	427
chloroform	443
trans-1,2-dichloroethylene	454
ethylene dichloride	460
carbon tetrachloride	502
1-chlorobutane	532
trichloroethylene	546
1,1,1-trichloroethane	568
tetrachloroethylene	574

Other Compound	Index
methyl alcohol	331
methyl formate	340
acetone	380
propanol	387
2-propanol	396
butane	400*
furan	407
ethyl formate	418
methylal	432
butanal	473
methylethylketone	476
pentane	500*
cyclopentanone	509
cyclohexane	511
thiophene	512
methyl acrylate	519
diacetyl	534
cyclohexanone	536
benzene	557
3-pentanone	558
2-pentanone	564
toluene	568
isooctane	570
pyridine	572
ethyl benzene	573
1-hexene	577
butyl acetate	578
hexane	600*

*Used as a standard.

TABLE 12. KOVATS RETENTION INDICES OF SELECTED COMPOUNDS ON 10% FFAP ON 80/100 MESH ACID-WASHED CHROMASORB W IN 20-FT X 1/8 IN STAINLESS STEEL AT 125°C

Chlorinated Compound	Index
1,1-dichloroethylene	738
benzyl chloride	770
2-chlorobutane	800
1-chlorobutane	855
trans-1,2-dichloroethylene	864
2-chloropentane	886
carbon tetrachloride	893
1,1-dichloroethane	896
1,1,1-trichloroethane	897
methylene dichloride	934
trichloroethylene	1004
chloroform	1025
tetrachloroethylene	1039
1-chlorohexane	1054
ethylene dichloride	1078

Other Compound	Index
heptane	700*
3-heptene	744
1-heptene	746
octane	800*
methyl acetate	844
1-octene	845
2-ethyl, 1-hexene	846
nonane*	900
ethyl acetate	901
methacrolein	904
methyl propanoate	921
methyl ethyl ketone	927
1-nonene	945
benzene	963
propyl acetate	988
decane	1000*
methyl butanoate	1000
1-decene	1044
ethyl butanoate	1048
toluene	1060
dioxane	1093
undecane	1100*

*Used as a standard.

TABLE 13. KOVATS RETENTION INDICES OF SELECTED COMPOUNDS ON PORAPAK T, 80/100 MESH IN 6.5-FT X 1/8-IN STAINLESS STEEL AT 140°C

Chlorinated Compound	Index
trans-1,2-dichloroethylene	550
carbon tetrachloride	553
1,1-dichloroethane	604
chloroform	625
n-butyl chloride	654
trichloroethylene	665
ethylene dichloride	666
tetrachloroethylene	736

Other Compound	Index
methanol	426
methyl formate	465
pentane	500*
furan	510
propanol	533
methylal	547
ethyl formate	561
isopropyl alcohol	576
4-methyl-2-pentene	582
4-methyl-1-pentene	584
hexane	600*
1-hexene	603
2-ethyl-1-butene	603
2-hexene	605
tetrahydrofuran	609
isooctane	618
cyclohexane	619
butanal	634
acetone	636
2-butanone	639
methylethylketone	644
ethyl acetate	646
benzene	658
thiophene	658
diacetyl	667
heptane	700*

*Used as a standard.

TABLE 14. KOVATS RETENTION INDICES OF SELECTED COMPOUNDS ON 15% TETRACYANOETHYLATED PENTAERYTHRITOL ON 60/80 MESH CHROMASORB P AW IN 16-FT X 1/8-IN STAINLESS STEEL

Chlorinated Compound	Index at 80°C	Index at 100°C
1,1-dichloroethylene	760	792
carbon tetrachloride	897	938
1,1-dichloroethane	940	994
methylene dichloride	956	1013
trichloroethylene	1009	1068
chloroform	1022	1090
tetrachloroethylene	1056	1105
1-chlorobutane	1105	
1-chlorohexane	1148	1148
1,2-dichloroethane	1131	1205
1,4-dichlorobutane		1303
chlorobenzene	1347	
1,3-dichloropropane	1352	

Other Compound	at 80°C	at 100°C
isooctane		683
heptane	700*	700*
nonane	900*	900*
1-nonene		972
ethyl formate		1014
2-propanol	1047	1046
1-decene		1070
ethyl acetate		1076
acetone	1009	1091
undecane	1100*	1100*
benzene	1039	1104
methyl acrylate		1125
2-methoxy ethanol		1155
methylethylketone	1087	1158
pyridine	1132	1158
propyl butanoate	1143	1170
thiophene	1102	1176
dodecane	1200*	1200*
toluene	1136	1201
monoethanolamine		1268
crotonaldehyde		1275
ethyl benzene		1281
m-xylene		1297

*Used as a standard.

TABLE 14. KOVATS RETENTION INDICES OF SELECTED COMPOUNDS ON 15% TETRACYANOETHYLATED PENTAERYTHRITOL ON 60/80 MESH CHROMASORB P AW IN 16-FT X 1/8-IN STAINLESS STEEL (Continued)

Other Compound	Index	
	at 80°C	at 100°C
p-xylene		1312
cumene		1318
o-xylene		1353
tetradecane		1400*
styrene		1419

*Used as a standard.

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APPENDIX A

METHOD FOR THE DETERMINATION OF HALOGENATED ORGANICS FROM STATIONARY SOURCES

METHOD 23. DETERMINATION OF HALOGENATED ORGANICS FROM STATIONARY SOURCES

INTRODUCTION

Performance of this method should not be attempted by persons unfamiliar with the operation of a gas chromatograph, nor by those who are unfamiliar with source sampling, as there are many details that are beyond the scope of this presentation. Care must be exercised to prevent exposure of sampling personnel to hazardous emissions.

1. Principle and Applicability

1.1 Principle. An integrated bag sample of stack gas containing one or more halogenated organics is subjected to gas chromatographic (GC) analysis, using a flame ionization detector (FID).

1.2 Applicability. The method is applicable to the measurement of halogenated organics such as carbon tetrachloride, ethylene dichloride, perchloroethylene, trichloroethylene, methylene chloride, 1-1-1 trichloroethane, and trichlorotrifluoroethane in stack gases only from specified processes. It is not applicable where the gases are contained in particulate matter.

2. Range and Sensitivity

The procedure described herein is applicable to the measurement of halogenated organics in the 0.1 to 200 ppm range. The upper limit may be extended by further calibration or by dilution of the sample.

3. Interferences

The chromatograph column with the corresponding operating parameters herein described has been represented as being useful for producing adequate resolution of halogenated organics. However, resolution

interferences may be encountered on some sources. Also, the chromatograph operator may know of a column that will produce a superior resolution of the particular compound of interest without reducing the response to that compound, as specified in Section 4.3.1.

In any event, the chromatograph operator shall select a column which is best suited to his particular analysis problem, subject to the approval of the Administrator. Such approval shall be considered automatic provided that confirming data produced through a demonstrably adequate supplemental analytical technique, such as analysis with a different column or G.C./mass spectroscopy, is available for review by the Administrator.

4. Apparatus

4.1 Sampling (see Figure 23-1).

4.1.1 Probe. Stainless steel, Pyrex[1] glass, or Teflon tubing according to stack temperature, each equipped with a glass wool plug to remove particulate matter if particulate matter is present.

4.1.2 Sample Line. Teflon, 6.4 mm outside diameter, of sufficient length to connect probe to bag. A new unused piece is employed for each series of bag samples that constitutes an emission test.

4.1.3 Male (2) and female (2) stainless steel quick connects, with ball checks (one pair without) located as shown in Figure 23-1.

4.1.4 Tedlar or aluminized Mylar bags, 100 liter capacity. To contain sample.

4.1.5 Rigid leakproof containers for 4.1.4, with covering to protect contents from sunlight.

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[1]Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

4.1.6 Needle Valve. To adjust sample flow rate.

4.1.7 Pump--Leak-Free. Minimum capacity 2 liters per minute.

4.1.8 Charcoal Tube. To prevent admission of halogenated organics to the atmosphere in the vicinity of samplers.

4.1.9 Flow Meter. For observing sample flow rate; capable of measuring a flow range from 0.10 to 1.00 liters per minute.

4.1.10 Connecting Tubing. Teflon, 6.4 mm outside diameter, to assemble sample train (Figure 23-1).

4.2 Sample Recovery.

4.2.1 Tubing. Teflon, 6.4 mm outside diameter, to connect bag to gas chromatograph sample loop. A new unused piece is employed for each series of bag samples that constitutes an emission test, and is to be discarded upon conclusion of analysis of those bags.

4.3 Analysis.

4.3.1 Gas Chromatograph. With FID, potentiometric strip chart recorder and 1.0 to 2.0 ml sampling loop in automatic sample valve. The chromatographic system shall be capable of producing a response to 0.1 ppm of the halogenated organic compound that is at least as great as the average noise level. (Response is measured from the average value of the baseline to the maximum of the waveform, while standard operating conditions are in use.)

4.3.2 Chromatographic Column. Stainless steel, 3.05 m x 3.2 mm, containing 20 percent SP-2100/0.1 percent Carbowax 1500 on 100/120 Supelcoport. Other columns can be used, provided that the precision and accuracy of the analysis of standards are not impaired. Information confirming that adequate resolution of the halogenated organic compound

peak is accomplished should be available. Adequate resolution is defined as an area overlap of not more than 10 percent of the halogenated organic compound peak by an interferent peak. Calculation of area overlap is explained in Appendix E, Supplement A: "Determination of Adequate Chromotographic Peak Resolution."

4.3.3 Flow Meters (2). Rotameter type, 0 to 100 ml/min capacity.

4.3.4 Gas Regulators. For required gas cylinders.

4.3.5 Thermometer. Accurate to one degree centigrade, to measure temperature of heated sample loop at time of sample injection.

4.3.6 Barometer. Accurate to 5 mm Hg, to measure atmospheric pressure around gas chromatograph during sample analysis.

4.3.7 Pump--Leak-free. Minimum capacity 100 ml/min.

4.3.8 Recorder. Strip chart type, optionally equipped with disc integrator or electronic integrator.

4.3.9 Planimeter. Optional, in place of disc or electronic integrator, for 4.3.8 to measure chromatograph peak areas.

4.4 Calibration. 4.4.2 through 4.4.6 are for section 7.1 which is optional.

4.4.1 Tubing. Teflon, 6.4 mm outside diameter, separate pieces marked for each calibration concentration.

4.4.2 Tedlar or Aluminized Mylar Bags. 50-liter capacity, with valve; separate bag marked for each calibration concentration.

4.4.3 Syringe. 25 µl, gas tight, individually calibrated, to dispense liquid halogenated organic solvent.

4.4.4 Syringe. 50 µl, gas tight, individually calibrated, to dispense liquid halogenated organic solvent.

4.4.5 Dry Gas Meter, With Temperature and Pressure Gauges. Accurate to ±2 percent, to meter nitrogen in preparation of standard gas mixtures, calibrated at the flowrate used to prepare standards.

4.4.6 Midget Impinger/Hot Plate Assembly. To vaporize solvent.

5. Reagents

It is necessary that all reagents be of chromatographic grade.

5.1 Analysis.

5.1.1 Helium Gas or Nitrogen Gas. Zero grade, for chromatographic carrier gas.

5.1.2 Hydrogen Gas. Zero grade.

5.1.3 Oxygen Gas or Air as Required by the Detector. Zero grade.

5.2 Calibration. Use one of the following options: either 5.2.1 and 5.2.2, or 5.2.3.

5.2.1 Halogenated organic compound, 99 mol percent pure, certified by the manufacturer to contain a minimum of 99 mol percent of the particular halogenated organic compound; for use in the preparation of standard gas mixtures as described in Section 7.1.

5.2.2 Nitrogen Gas. Zero grade, for preparation of standard gas mixtures as described in Section 7.1.

5.2.3 Cylinder Standards (3). Gas mixture standards (200, 100, and 50 ppm of the halogenated organic compound of interest, in nitrogen) for which the gas composition has been certified with an accuracy of ±3 percent or better by the manufacturer. The manufacturer must have recommended a maximum shelf life for each cylinder so that the concentration

does not change by greater than ± 5 percent from the certified value. The date of gas cylinder preparation, certified concentration of the halogenated organic compound and recommended maximum shelf life must have been affixed to the cylinder before shipment from the gas manufacturer to the buyer. These gas mixture standards may be directly used to prepare a chromatograph calibration curve as described in Section 7.2.2.

5.2.3.1 Cylinder Standards Certification. The concentration of the halogenated organic compound in nitrogen in each cylinder must have been certified by the manufacturer by a direct analysis of each cylinder using an analytical procedure that the manufacturer had calibrated on the day of cylinder analysis. The calibration of the analytical procedure shall, as a minimum, have utilized a three-point calibration curve. It is recommended that the manufacturer maintain two calibration standards and use these standards in the following way: (1) a high concentration standard (between 200 and 400 ppm) for preparation of a calibration curve by an appropriate dilution technique; (2) a low concentration standard (between 50 and 100 ppm) for verification of the dilution technique used. If the difference between the apparent concentration read from the calibration curve and the true concentration assigned to the low concentration standard exceeds 5 percent of the true concentration, determine the source of error and correct it, then repeat the three-point calibration.

5.2.3.2 Establishment and Verification of Calibration Standards. The concentration of each calibration standard must have been established by the manufacturer using reliable procedures. Additionally, each calibration standard must have been verified by the manufacturer by

one of the following procedures, and the agreement between the initially determined concentration value and the verification concentration value must be within ± 5 percent: (1) verification value determined by comparison with a gas mixture prepared in accordance with the procedure described in Section 7.1.1 and using 99 mol percent of the halogenated organic compounds, or (2) verification value obtained by having the calibration standard analyzed by the National Bureau of Standards, if such analysis is available. All calibration standards must be reverified on a time interval consistent with the shelf life of the cylinder standards sold.

5.2.4 Audit Cylinder Standards (2). Gas mixture standards identical in preparation to those in Section 5.2.3 (the halogenated organic compounds of interest, in nitrogen), except the concentrations are only known to the person supervising the analysis of samples. The concentrations of the audit cylinders should be: one low concentration cylinder in the range of 25 to 50 ppm, and one high concentration cylinder in the range of 200 to 300 ppm. When available, audit cylinders may be obtained by contacting: EPA, Environmental Monitoring and Support Laboratory, Quality Assurance Branch (MD-77), Research Triangle Park, North Carolina 27711. If audit cylinders are not available at EPA, an alternate source must be secured.

6. Procedure

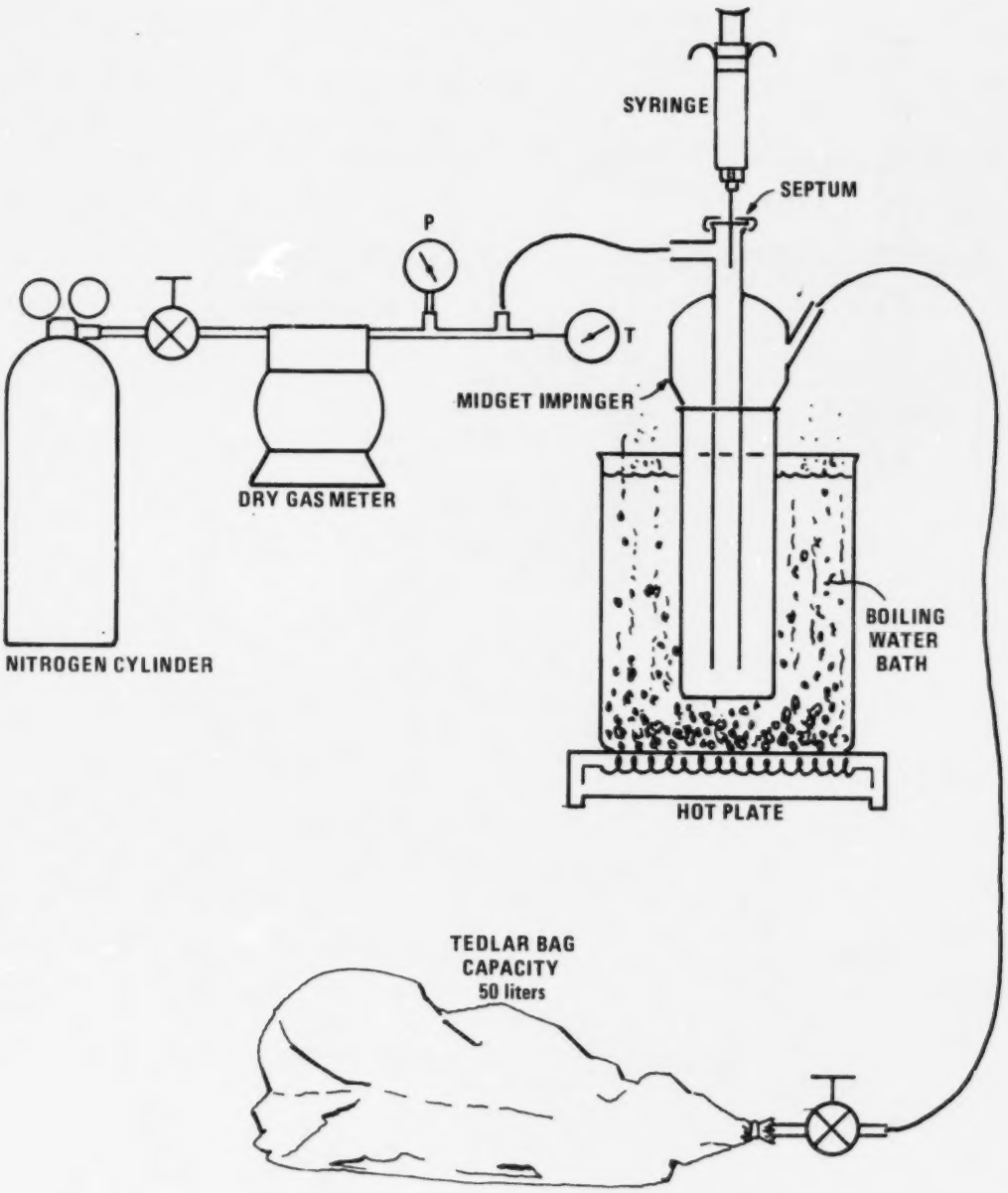
6.1 Sampling. Assemble the sample train as in Figure 23-1. Perform a bag leak check according to Section 7.3.2. Join the quick connects as illustrated, and determine that all connections between the bag and the probe are tight. Place the end of the probe at the

centroid of the stack and start the pump with the needle valve adjusted to yield a flow of 0.5 lpm. After a period of time sufficient to purge the line several times has elapsed, connect the vacuum line to the bag and evacuate the bag until the rotameter indicates no flow. At all times, direct the gas exiting the rotameter away from sampling personnel. Then reposition the sample and vacuum lines and begin the actual sampling, keeping the rate constant. At the end of the sample period, shut off the pump, disconnect the sample line from the bag, and disconnect the vacuum line from the bag container. Protect the bag container from sunlight.

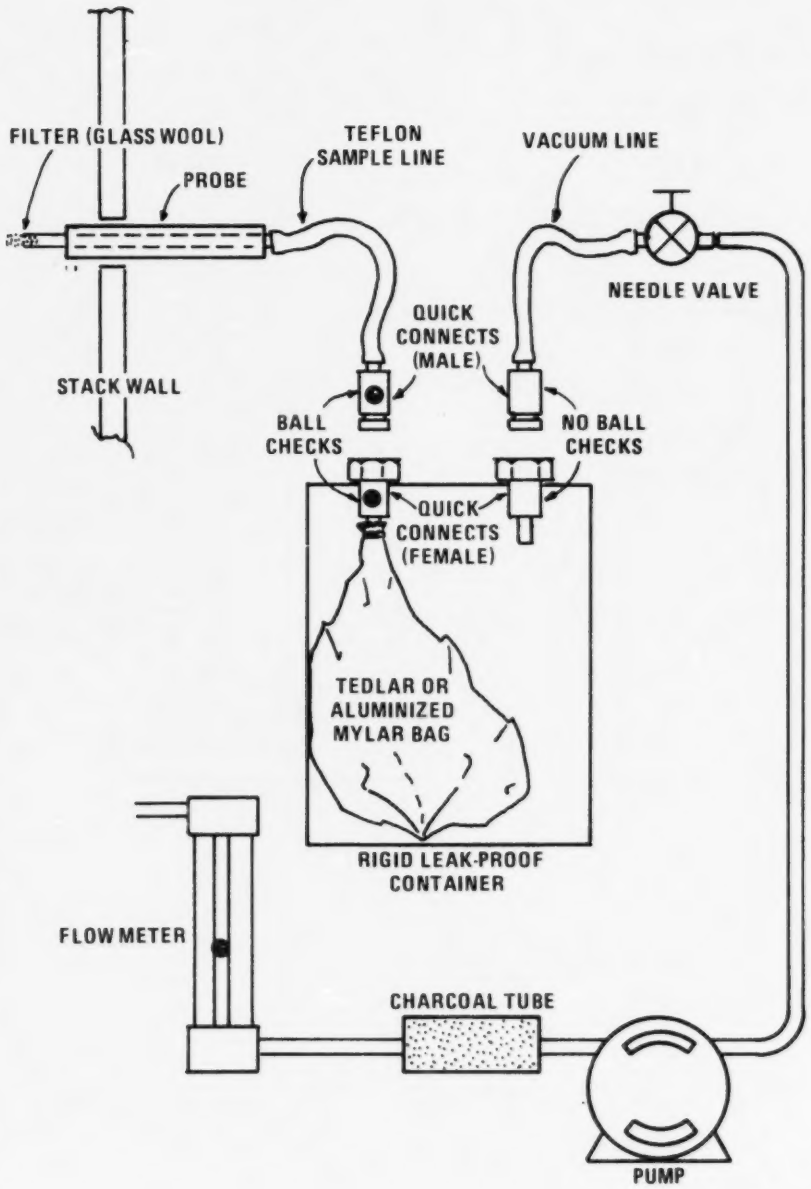
6.2 Sample Storage. Sample bags must be kept out of direct sunlight and must be protected from heat. Analysis must be performed within 1 day of sample collection for methylene chloride, ethylene dichloride and trichlorotrifluoroethane. Analysis of perchloroethylene, trichloroehtylene, 1, 1, 1-trichloroethane and carbon tetrachloride must be performed within 2 days.

6.3 Sample Recovery. With a new piece of Teflon tubing identified for that bag, connect a bag inlet valve to the gas chromatograph sample valve. Switch the valve to receive gas from the bag through the sample loop. Arrange the equipment so the sample gas passes from the sample valve to a 0-100 ml/min rotameter with flow control valve followed by a charcoal tube and a 0-1 inch w.g. pressure gauge. Sample flow may be maintained either by a vacuum pump or container pressurization if the collection bag remains in the rigid container. After sample loop purging is ceased, allow the pressure gauge to return to zero before activating the gas sampling valve.

TRAIN FOR PREPARATION OF SAMPLES



INTEGRATED - BAG SAMPLING TRAIN



6.4 Analysis. Set the column temperature to 100° C, and the detector temperature to 225° C. When optimum hydrogen and oxygen flow rates have been determined, verify and maintain these flow rates during all chromatograph operations. Using zero helium or nitrogen as the carrier gas, establish a flow rate in the range consistent with the manufacturer's requirements for satisfactory detector operation. A flow rate of approximately 20 ml/min should produce adequate separations. Observe the base line periodically and determine that the noise level has stabilized and that base line drift has ceased. Purge the sample loop for thirty seconds at the rate of 100 ml/min, then activate the sample valve. Record the injection time (the position of the pen on the chart at the time of sample injection), the sample number, the sample loop temperature, the column temperature, carrier gas flow rate, chart speed and the attenuator setting. Record the laboratory pressure. From the chart, note the peak having the retention time corresponding to the halogenated organic compound as determined in Section 7.2.1. Measure the halogenated organic compound peak area, A_m, by use of a disc integrator, electronic integrator, or a planimeter. Record A_m and the retention time. Repeat the injection at least two times or until two consecutive values for the total area of the peak do not vary more than 5 percent. The average value for these two total areas will be used to compute the bag concentration.

6.5 Measure the ambient temperature and barometric pressure near the bag. From a water saturation vapor pressure table, determine and record the water vapor content of the bag as a decimal figure. (Assume the relative humidity to be 100 percent unless a lesser value is known.)

7. Standards, Calibration, and Quality Assurance

7.1 Standards.

7.1.1 Preparation of Standard Gas Mixtures. (Optional-delete if cylinder standards are used.) Assemble the apparatus shown in Figure 232. Check that all fittings are tight. Evacuate a 50-liter Tedlar or aluminized Mylar bag that has passed a leak check (described in Section 7.3.2) and meter in about 50 liters of nitrogen. Measure the barometric pressure, the relative pressure at the dry gas meter, and the temperature at the dry gas meter. Refer to Table 23-1. While the bag is filling, use the 50 μl syringe to inject through the septum on top of the impinger, the quantity required to yield a concentration of 200 ppm. In a like manner, use the 25 μl syringe to prepare bags having approximately 100 and 50 ppm concentrations. To calculate the specific concentrations, refer to Section 8.1. Tedlar bag gas mixture standards of methylene chloride, ethylene dichloride, and trichlorotrifluoroethane may be used for 1 day; trichloroethylene and 1, 1,1-trichloroethene for 2 days; perchloroethylene and carbon tetrachloride for 10 days from the date of preparation. (Caution: Contamination may be a problem when a bag is reused if the new gas mixture standard is a lower concentration than the previous gas mixture standard.)

7.2 Calibration.

7.2.1 Determination of Halogenated Organic Compound Retention Time. This section can be performed simultaneously with Section 7.2.2. Establish chromatograph conditions identical with those in Section 6.3, above. Determine proper attenuator position. Flush the sampling loop with zero helium or nitrogen and activate the sample valve. Record the

TABLE 23-1. INJECTION VALUES FOR PREPARATION OF STANDARDS. (Optional, see Section 7.1.1)

Compound	Molecular Weight (M)	Density at 293° A (D)	µl Liquid Required in 50 l N_2 for Approximate Concentration of: 200 ppm	100 ppm	50 ppm
Perchloroethylene C_2Cl_4	165.85	1.6230	42.5	21.2	10.6
Trichloroethylene C_2HCl_3	131.40	1.4649	37.3	18.6	9.3
1,1,1-Trichloroethane $C_2H_3Cl_3$	133.42	1.4384	38.6	19.3	9.6
Methylene Chloride CH_2Cl_2	84.94	1.3255	26.6	13.3	6.7
Trichlorotrifluoroethane $C_2Cl_3F_3$	187.38	1.5790	49.3	24.7	12.3
Carbon Tetrachloride CCl_4	153.84	1.5940	40.1	20.1	10.0
Ethylene Dichloride $C_2H_4Cl_2$	98.96	1.2569	32.7	16.4	8.2

injection time, the sample loop temperature, the column temperature, the carrier gas flow rate, the chart speed and the attenuator setting. Record peaks and detector responses that occur in the absence of the halogenated organic. Maintain conditions (with the equipment plumbing arranged identically to Section 6.3), flush the sample loop for 30 seconds at the rate of 100 ml/min with one of the halogenated organic compound calibration mixtures, and activate the sample valve. Record the injection time. Select the peak that corresponds to the halogenated organic compound. Measure the distance on the chart from the injection time to the time at which the peak maximum occurs. This distance divided by the chart speed is defined as the halogenated organic compound peak retention time. Since it is possible that there will be other organics present in the sample, it is very important that positive identification of the halogenated organic compound peak be made.

7.2.2 Preparation of Chromatograph Calibration Curve. Make a gas chromatographic measurement of each standard gas mixture (described in Section 5.2.3 or 7.1.1) using conditions identical with those listed in Sections 6.3 and 6.4. Flush the sampling loop for 30 seconds at the rate of 100 ml/min with one of the standard gas mixtures and activate the sample valve. Record C_c, the concentration of halogenated organic injected, the attenuator setting, chart speed, peak area, sample loop temperature, column temperature, carrier gas flow rate, and retention time. Record the laboratory pressure. Calculate A_c, the peak area multiplied by the attenuator setting. Repeat until two consecutive injection areas are within 5 percent, then plot the average of those two

values versus C_c. When ther other standard gas mixtures have been similarly analyzed and plotted, draw a straight line through the points. Perform calibration daily, or before and after each set of bag samples, whichever is more frequent.

7.3 Quality Assurance.

7.3.1 Analysis Audit. Immediately after the preparation of the calibration curve and prior to the sample analyses, perform the analysis audit described in Appendix E, Supplement B: "Procedure for Field Auditing GC Analysis."

7.3.2 Bag Leak Checks. While performance of this section is required subsequent to bag use, it is also advised that it be performed prior to bag use. After each use, make sure a bag did not develop leaks as follows: to leak check, connect a water manometer and pressurize the bag to 5-10 cm H_2O (2-4 in. H_2O). Allow to stand for 10 minutes. Any displacement in the water manometer indicates a leak. Also, check the rigid container for leaks in this manner. (Note: an alternative leak check method is to pressurize the bag to 5-10 cm H_2O or 2-4 in. H_2O and allow to stand overnight. A deflated bag indicates a leak.) For each sample bag in its rigid container, place a rotameter in line between the bag and the pump inlet. Evacuate the bag. Failure of the rotameter to register zero flow when the bag appears to be empty indicates a leak.

8. Calculations

8.1 Optional Standards Concentrations. Calculate each halogenated organic standard concentration prepared in accordance with Section 7.1.1 as follows:

$$C_c = \frac{B\mu l \ \frac{D\ \mu g}{\mu l} \ \frac{10^3\ \mu g}{mg} \ \frac{\mu g\ mole}{M\ \mu g} \ \frac{24.055\ \mu l}{\mu g\ mole} \ 10^6}{V_m\ Y\ \frac{10^6\ \mu l}{l} \ \frac{293}{T_m} \ \frac{P_m}{760}}$$

$$= \frac{\frac{BD}{M}\ (24.055 \times 10^3)}{V_m\ Y\ \frac{293}{T_m}\ \frac{P_m}{760}} \qquad \text{Equation 23-1}$$

Where:

C_c = Standard concentration in ppm.

B = Number of μl of injected.

V_m = Gas volume measured by dry gas meter in liters.

Y = Dry gas meter calibration factor.

P_m = Absolute pressure of the dry gas meter, mm Hg.

T_m = Absolute temperature of the dry gas meter, °A.

D = Density of compound at 293° A.

M = Molecular weight of compound.

24.055= Ideal gas at 293° A, 760 mm Hg.

10^6 = Conversion factor, ppm.

8.2 Sample Concentrations. From the calibration curve described in Section 7.2.2 above, select the value of C_c that corresponds to A_c. Calculate C_s as follows:

$$C_s = \frac{C_c P_r T_i}{P_i T_r (1-S_{wb})} \qquad \text{Equation 23-2}$$

Where:

S_{wb} = The water vapor content of the bag sample, as analyzed.

C_s = The concentration of the halogenated organic in the sample in ppm.

C_c = The concentration of the halogenated organic indicated by the gas chromatograph, in ppm.

P_r = The reference pressure, the laboratory pressure recorded during calibration, mm Hg.

T_i = The sample loop temperature on the absolute scale at the time of analysis, °A.

P_i = The laboratory pressure at time of analysis, mm Hg.

T_r = The reference temperature, the sample loop temperature recorded during calibration, °A.

9. References

1. Feairheller, W. R.; Kemmer, A.M.; Warner, B. J.; and Douglas, D. Q. "Measurement of Gaseous Organic Compound Emissions by Gas Chromatography," EPA Contract No. 68-02-1404, Task 33 and 68-02-2818, Work Assignment 3. January 1978. Revised August, 1978, by EPA.

2. Bullein 747. "Separation of Hydrocarbons" 1974. Supelco, Inc. Bellefonte, Pennsylvania 16823.

3. Communication From Joseph E. Knoll. Perchloroethylene Analysis by Gas Chromatography. March 8, 1978.

4. Communication From Joseph E. Knoll. Test Method for Halogenated Hydrocarbons. December 20, 1978.